FIELD MODIFICATION FORM
LOWER PASSAIC RIVER RESTORATION PROJECT

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Activity: Radiochemistry Dating of Dundee Lake High Resolution Sediment Core Samples

Requested Modifications: Malcolm Pirnie collected high resolution sediment cores from Dundee Lake on January 11, 2007. Selected samples were submitted for radiochemistry analyses (Cs-137 on all sediment segments plus Be-7 on the surface sediment slices only) to STL in order to date the core sediment layers. Due to the small volume of the sediment sample available, background levels and longer than anticipated counting times required, STL has been challenged to achieve sufficiently low detection limits on all the samples particularly for the Be-7 measurements on the surface sediments.

We propose to have STL send sediment samples (already prepared and dried by STL) which we have selected to Dr. Richard Bopp of Rensselaer Polytechnic Institute (RPI) for radiochemistry analyses for Be-7 and Cs-137. Dr. Bopp has extensive experience dating sediment samples and previously dated sediment cores from both the Hudson River and the Passaic River. Dr. Bopp's laboratory is equipped with Gamma Spectrometer instrumentation with a detector configuration especially designed for counting very small volume sediment samples. The RPI radiochemistry lab is well suited for low level environmental measurements, since they does not handle higher level radiological materials which might add to their background counts.

When comparing the data between the laboratories we would expect that the results agree within the uncertainty (2 sigma). If there is a conflict in the data obtained by STL and Dr. Bopp, we will use the data which is reported with the smallest error based upon counting statistics.

Attached is a copy of the Gamma Spectrometer method which Dr. Bopp proposes to employ to perform radiochemistry analyses. This is the same methodology employed in the past for similar Hudson River studies.

Rationale: The proposed analyses at RPI will improve the quality of the radiochemistry dating of the Dundee Lake sediment cores. Since Be-7 has a relatively short half life (53.44 days), we request that this action be approved, so that any confirmatory measurements can be made as soon as possible.

Attachment: Radionuclides Method

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Attachment 1

RADIONUCLIDES: BERYLLIUM-7 CESIUM-137, LEAD-210, LEAD 214, BISMUTH-214, and POTASSIUM-40: RPI METHOD

1.0   Scope and Application

1.1   The method describes the procedure to determine the activities of several radionuclides in sediment and soil samples. These radionuclides are derived from natural and anthropogenic sources. The technique is non-destructive. This procedure will be performed at the Rensselaer Polytechnic Institute (RPI).

2.0   Method Summary

2.1   A sample of river sediment, 5 to 120g, is dried in a controlled atmosphere and then homogenized using a mortar and pestle. The weight of the sample is determined and recorded. The homogenized sample is placed in a plastic counting tube (4 cc volume Wheaton Omnivial®), and the tube is placed in the well of a gamma spectrometer. The presence of a given radionuclide is determined from its gamma decay energy signature. The level of activity for a given radionuclide is proportional to the number of decays detected per unit time.

2.2   The principal radionuclides to be measured are beryllium -7 and cesium -137. Data on other radionuclides including lead-210, lead-214, bismuth -214, cesium-134, cobalt-60, actinium-228 and potassium-40 will also be obtained.

2.3   Method interferences may be caused by cosmic radiation if sufficient shielding of the sample and counter is not provided.

3.0   Apparatus and Materials

3.1   Drying Chamber – The drying chamber consists of an incubator maintained at 35°C or less. The "PCB-free" atmosphere in the incubator is maintained by using a purging system which consists of a clean air source and a florisil® column for removing PCBs and other organochlorines including PCDD/Fs from air. The use of this drying system ensures that the samples are suitable for gamma spectrometry as well as for long term storage for potential PCB and/or PCDD/F analysis at some time in the future.

3.2   Precision Balance. The balance must be capable of weighing at 200.0 ± 0.1g.

3.3   Gamma spectrometer. The spectrometer consists of an intrinsic germanium crystal (Ortec GWL-120) capable of measuring gamma decay radiation energy at high resolution. The detector is connected to a computer-based data logger for final data output and calculations.

4.0   Reagents

Standards – Detector efficiency was calibrated using an National Bureau of Standards (NBS) sediment standard (River sediment NBS 4350B), a liquid NBS standard (NBS 4953-C) that was used to prepare spiked sediments (G-standards), and secondary standards (D-standards) prepared at the Lamont-Doherty Earth Observatory and calibrated to NBS standards.

5.0   Initial Calibration

Complete calibrations of the system involving analyses of dozens of standards and blanks were carried out in 1995 and 1996. Since that time analyses of a few dozen standards and several blanks per year have been carried out as a continuous calibration check. Complete data from all these analyses is available in electronic format.

6.0   Procedure

6.1   Dry the sectioned sediment core samples at low temperature in the drying chamber. Dry samples are necessary for the gamma counting method because all of the detector calibrations are performed with dry materials. This also permits the highest and most uniform counting efficiencies to be achieved by eliminating absorption of gamma rays by variable quantities of water in the samples.

6.2   Grind the dry sediments to a fine powder with a large mortar and pestle. This step is essential to achieving a well-mixed uniform sample texture for gamma counting and for representative subsampling for other analyses.

6.3   Remove the material necessary for other analyses. Determine the remaining sample weight and place in a counting tube. Seal the dry sediment powder in the tube when it has been filled to the bottom of the cap to obtain a reproducible geometry for gamma spectrometry and to permit the daughter products of Rn-222 (half-life = 3.8 days) and Rn-220 (half-life = 54 seconds), both of which are gases, to achieve secular equilibrium with the critical gamma-emitting daughter products in the uranium and thorium decay series.

6.4   If data on Rn-222 daughters is required (Bi-214 or Pb-214 for example, which are used in the determination of supported Pb-210), set the sealed tubes aside for a minimum of approximately 5 half-lives of Rn-222 (20

days) to permit a achievement of secular equilibrium of U-238 decay series nuclides.

6.5   Place a sealed tube into the well of the intrinsic germanium detector.

6.6   Start accumulation of the spectrum of gamma emissions as a function of energy of each gamma ray detected.

6.7   Accumulation of the gamma spectrum should be terminated after enough counts have been recorded for the critical nuclides, Cs-137 and Be-7, to yield a statistical counting error of $\leq 10\%$, (1σ) or until 8 hrs of counting time have elapsed. Technical judgment may be used in the final determination of counting endpoints, especially for samples with extremely low activity levels.

6.8   Save the spectrum along with other relevant data necessary for calculation of the radionuclide activities per unit weight of sample: sample weight (dry), sample collection date, sample counting date, total counting time, code information for sample identification (e.g. core mile point, depth interval, laboratory control number) in electronic format (.rtf files, Ortec Maestro software)

6.9   Reduce the data discussed above in the calculation program to obtain concentrations for each radionuclide of interest, expressed in terms of activity units, picoCuries (pCi) per kilogram of dry weight of sediment. One pCi is equivalent to 2.22 disintegrations per minute (dpm), 0.037 Becquerels (1 Becquerels = 1 disintegration per second, dps). One Curie equals the number of decays per gram of pure radium-226, and one pCi equals 10^{12} Ci.

6.10   Any remaining dry sediment powder can be saved indefinitely in sealed aluminum cans or in pre-fired (450°C overnight) glass vials with Teflon lined screw caps without risk of contamination or need to retain at low temperature to prevent microbial alteration of any important labile constituents. These containers can be opened at a later time for further sampling and resealed.

7.0   Calculations

7.1   Counting Statistics – The rough counting statistics error is calculated as given below.

$$\% \ error = \frac{\sqrt{Total \ Sample \ Counts}}{Total \ Sample \ Counts} \ x \ 100\%$$

$$= \frac{1}{\sqrt{Total \ Sample \ Counts}} \ x \ 100\%$$

Counting statistics errors will be reported down to 5% error.

7.2 The complete calculation of the sample activity for an individual radionuclide is given by the following example for Cs-137 in a laboratory standard. Note that the branching ratio is obtained form the scientific literature and is the ratio of the proportion of decays represented by the measured gamma radiation to all decays undergone by the radionuclide. For the example, 0.851 or 85.1% of all Cs-137 atoms decay via the gamma decay mode at 661.6-KeV.

Sample SLOSH III 1000 I-2 (internal standard):

Counts in peak	=	7773 (13 channels, ch.)
Counts in background	=	946 (20 channels)
Count time	=	1387 minutes
Sediment weight	=	92 grams
Detector efficiency	=	0.012372576
Branching ratio	=	0.851
cpm	=	counts per minute
dpm	=	decays per minute

$$(1) \ cpm \ in \ peak = \frac{7773 \pm \sqrt{7773}}{1387} = 5.60 \pm 0.06$$

$$(2) \ Bkg./20 \ ch. = 946; \ bkg./13 \ ch. = 615$$

$$cpm \ in \ bkg. = \frac{615 \pm \sqrt{615}}{1387} = 0.44 \pm 0.018$$

$$(3)\ Net\ cpm\ in\ peak = (5.6 - 0.44) \pm \sqrt{(0.06)^2 + (0.018)^2} = 5.16 \pm 0.066$$

$$(4)\ Net\ cpm\,/\,g = \frac{5.16 \pm 0.066}{92} = 0.056 \pm 0.0007\ (error\ 1.3\%)$$

$$(5)\ Net\ dpm\,/\,g = \frac{cpm\,/\,g}{Eff}\ x\ \frac{1}{B.R.} = \frac{0.056}{0.012372576} = \frac{1}{0.851} = 5.33$$

$$(6)\ Error\ calculation\ for\ dpm\,/\,g\ must\ include:$$

$$sample\ counting\ error\ (1.3\%)$$
$$std.\ counting\ error\ (1.4\%)$$
$$statistical\ error\ in\ std.\ (0.2\%)\ given\ with\ std.$$

$$\%\ error = \sqrt{(1.3\%)^2 + (1.4\%)^2 + (0.2\%)^2} = \sim 2\%$$

$$(7)\ 5.33\ dpm\,/\,g \pm (5.33\ x\ 2\%) = 2.33 \pm 0.107\ dpm\,/\,g$$

$$(8)\ Coversation\ to\ pCi\,/\,kg: \frac{(1000g\,/\,kg)}{(222\ dpm\,/\,pCi)}\ (5.33 \pm 0.107\ dpm\,/\,g) = 2400 \pm 48\ pCi\,/\,kg$$

7.3 For radionuclides exhibiting two or more modes of gamma decay, the activity will be reported as the mean of each individual mode of decay calculated in pCi/kg.

7.4 All short lived isotopes (half life less than 50 years) must be corrected to the date of sample collection using the following formula:

$$A_o = \frac{A}{e^{-2(t-t_o)}}$$

where: A_o = activity of the radionuclide at time of collection (t_o).

A = measured activity of the radionuclide.

t_o = time of collection.

t = time of analysis.

Λ = decay constant for the radionuclide in units consistent with t and t_o.

8.0 Precision and Accuracy

8.1   Because of the low level of activity for some radionuclides of interest and the small sample size, precision and accuracy will be constrained by time limitations.

8.2   All sediment samples should be counted for at least 8 hours each or until the statistical counting error is ≤ 10% for both Be-7 and Cs-137. No other radionuclides will be used to determine the sample counting end point; however, technical judgment may be used, especially incases where samples have extremely low activity levels. For samples where the ≤ 10% threshold is reached, anticipated overall precision and accuracy is 20% However, no sample radionuclide results will be rejected based upon counting a statistics alone. The final decision as to data usability will be depend upon the interpretation of the radionuclide chronologies for an entire core.

8.3   The *minimum* detection limits for Cs-137 and Be-7 are 60 pCi/kg and 300 pCi/kg, respectively.

9.0   Quality Control

9.1   Background Measurement - Background measurements will be made using empty sample vials on a regular basis, roughly once every two months. Any background analysis that deviates by more than two standard deviations from the long term mean used in the data reduction program will be repeated immediately. If the deviation persists, background levels used in the program will be adjusted. It should be noted that except for Pb-210, such deviation in background has not been encountered a single time in the past ten years. In the case of Pb-210, the problem was solved by cleaning the dust that had accumulated inside the detector shield.

9.2   Continuing Calibration Verification Certified standards or secondary standards traceable to certified standards such as those mentioned in Section 4.0, will be run once for every twenty samples.

9.3   If a CCV standard analysis deviates by more than two standard deviations from the certified or accepted activities, the analysis will be repeated immediately. If the deviation persists, the instrument may require recalibration. Recalibration as a result of unacceptable reproducibility of standard analyses has not been required at any time in the past ten years.

9.4   Duplicate Analysis - Duplicate analyses will be performed for one in every twenty samples. The results are considered acceptable if the values for Cs-137 and Be-7 overlap when reported with their respective 1σ standard deviations. If the difference is greater, a third replicate analysis will be performed on that sample and an additional duplicate analysis will be performed on another sample from the batch of twenty.

10.0 References

10.1 Olsen, C.R., Radionuclides, Sedimentation and the Accumulation of Pollutants in the Hudson Estuary, Ph.D. dissertation, Columbia University, 343 pp., 1979.

10.2 Olsen, C.R., H.J. Simpson, T.-H. Peng, R.F. Bopp and R.M. Trier, Sedimentation mixing and accumulation rate effects on radionuclide depth profiles in Hudson estuary sediments, J. Geophvs. Res. 86, 11020-1 1028, 1981.